1 457 157

# PATENT SPECIFICATION

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## (54) MOULDABLE, ELECTRICALLY-CONDUCTIVE THERMOPLASTIC RESIN COMPOSITION

(71) We, MITSUBISHI RAYON COMPANY, LIMITED, a Japanese company, of No. 8, Kyobashi 2-Chome, Chuo-Ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a thermoplastic resin composition consisting essentially of carbon black, a polyolefin resin having good affinity for carbon black and another thermoplastic resin having poor affinity for carbon black and polyolefin resin, which composition can be moulded into plastics articles having superior electrical properties.

A mixture of carbon black having good electrical conductivity and one of certain thermoplastic resins is known to provide a thermoplastic resin composition capable of being moulded into plastic articles having superior electrical properties. However, in order to prepare a moulded plastics article having superior electrical properties from such a resin composition, it is necessary to use a very large amount of carbon black as compared with thermoplastic resin. However, a thermoplastic resin composition containing such a large quantity of carbon black has a markedly increased viscosity when molten, and its mouldability is reduced. At the same time, the resulting moulded article is subject to brittle fracture, and its mechanical properties are extremely impaired.

Various attempts have been made to use a thermoplastic elastomer having superior flexibility or a rubber as a matrix component in order to improve these mechanical properties and when such a moulded plastics article is used substantially at room temperature, its electrical properties are almost stable. However, when the article is used at a relatively high temperature, the volume inherent resistivity of the moulded article is greatly increased as a result of even a slight change in temperature, and the electrical conductivity of the moulded article tends to be decreased abruptly, making it impossible to use the moulded article at high temperatures. Furthermore, when such a moulded plastics article is used at high temperatures, it fatigues due to heat and the volume inherent resistivity of the moulded article gradually increases so that it cannot be used as an electrically-conductive moulded plastics article.

An object of the present invention is to provide a thermoplastic resin composition capable of being formed into a moulded plastics article with good mouldability, which has a low volume inherent resistivity and superior mechanical properties, and in which the extent of changes in volume inherent resistivity is reduced even when there is a change in temperature during the use of the moulded plastics article at a high temperature range. As a result, it has been found that a thermoplastic resin composition capable of achieving the above object can be obtained by a combination of a polyolefin resin, carbon black, and another thermoplastic resin having poor affinity for the polyolefin resin and the carbon black in specific proportions.

Accordingly this invention provides a mouldable, electrically conductive thermoplastic resin composition, the composition consisting essentially of (A) 95 to 30% by weight of a resin composition consisting of (i) 100 parts by weight of a polyolefin resin having good affinity for carbon black and (ii) 5 to 900 parts by weight of a thermoplastic resin having poor affinity (as herein defined) for the polyolefin resin and for carbon black, said thermoplastic resin being at least one of a polyamide, a polyester, polystyrene, and poly-(methyl methacrylate); and (B) 5 to 70% by weight of carbon black.

Specific examples of polyolefin resins having good affinity for carbon black as used in the practice of this invention are a homopolymers of a monomer having from 2 to 5 carbon

atoms in the main chain, such as ethylene, propylene, butene-1, pentene-1 or 4-methylpentene-1, and copolymers of these monomers in any proportion. These polymers can be used either alone or as an admixture of two or more. A suitable mean molecular weight is from 1,000 to 50,000, preferably from 10,000 to 40,000. The use of polyethylene or polypropylene is especially preferred in view of its affinity for carbon black, the mouldability of the thermoplastic resin composition, and the electrical and mechanical properties of the resulting moulded article.

Suitable polyamides having poor affinity both for the polyolefin and for the carbon black are those (e.g., having a mean molecluar weight of from 1,000 to 50,000, preferably from 10,000 to 25,000) obtained by the polycondensation of a dicarboxylic acid represented by the general formula HOOCRCOOH (wherein R represents an alkylene group or an arylene group, such as a phenylene group, having from 2 to 10 carbon atoms) such as succinic acid, adipic acid, sebacic acid, phthalic acid, isophthalic acid or terephthalic acid, and a diamine represented by the general formula $H_2NR'NH_2$ (wherein R' represents an alkylene group or an unsubstituted or substituted arylene group, such as a phenylene group, having from 2 to 1 0carbon atoms) such as ethylene diamine, propylene diamine, hexamethylene diamine, decamethylene diamine, undecamethylene diamine or xylene diamine and homopolymers (e.g., having a mean molecular weight of from 1,000 to 50,000, preferably from 10,000 to 25,000) of capramide, ω-aminoheptanoic acid or undecanamide, or their polycondensates. Suitable polyesters (e.g., having a mean molecular weight of from 5,000 to 50,000, preferably from 8,000 to 30,000) are obtained by the polycondensation of a dicarboxylic acid, as described above, and a diol represented by the general formula HOR"OH (wherein R" represents an alkylene group having from 2 to 10 carbon atoms) such as ethylene glycol, propylene glycol, 1,3-butanediol or 1,4-pentanediol. The polystyrene preferably has an intrinsic viscosity [$\eta$], as measured in methyl ethyl ketone at 25° C, of from 0.4 to 1.5; and the poly(methyl methacrylate) preferably has an intrinsic viscosity [$\eta$], as measured in chloroform at 25° C, of from 0.3 to 1.5. These resins can be used either alone or in admixture of at least two thereof.

"Poor affinity" as the term is used herein to describe the relationship between the polyolefin and the other thermoplastic resins exists if (1) a strand, which is obtained by melt-extruding the above resin mixture under a load of 2.16 Kg at a temperature of 250 to 280° C using a Melt Indexer, shows a Barus effect, or (2) the relationship between the proportion of the components of the resin mixture and the Melt Index value obtained deviates from additive linearity. Furthermore, "poor affinity" as the term is used herein to describe the relationship between the matrix resin and the carbon black exists if a film, which is obtained by adding carbon black in an amount of 1 wt. % to the matrix resin, mixing at a temperature of 250 to 280° C for 5 minutes using a Plastograph and then making a film at a temperature of 250 to 280° C, contains a number of condensed agglomerates of carbon black having a size of greater than 100$\mu$ upon observation with a microscope. Correspondingly, "good affinity" exists if the conditions described above are not fulfilled.

It is essential that the above thermoplastic resin be added in an amount of from 5 to 900 parts by weight per 100 parts by weight of the polyolefin resin. When a thermoplastic resin composition containing the other thermoplastic resin in an amount of less than 5 parts by weight is used, it is difficult to obtain moulded plastics articles having superior electrical and mechanical properties with good mouldability from such a thermoplastic resin composition, regardless of efforts made strictly to select and control the amount of carbon black. When it is desired to improve only the electrical properties of the moulded plastics articles, a large amount of carbon black can be added to the thermoplastic resin. However, the resulting thermoplastic resin composition has poor melt-mouldability, and it is difficult to prepare moulded articles of a desired shape. In addition, the mechanical properties, especially the fatigue-resistance during use, of the resulting moulded plastics articles are insufficient. On the other hand, when a thermoplastic resin composition containing the other thermoplastic resin in an amount exceeding 900 parts by weight is used, regardless of efforts made to strictly select and control the amount of carbon black used as an improving agent for the electrical properties of the composition, the carbon black is not dispersed sufficiently in a plastics article moulded from the thermoplastic resin composition to obtain improvements in its electrical properties. In other words, the state of dispersion of carbon black does not promote a reduction in the volume inherent resistivity of the moulded plastics article. Accordingly, it is impossible to produce moulded plastics articles having good electrical properties from such a thermoplastic resin composition. Furthermore, when such an article is used at a relatively high temperature, e.g., above 50° C, its volume inherent resistivity changes greatly even when there is a slight change in temperature, and the article does not exhibit stable electrical characteristics.

Specific examples of the carbon black used in the practice of this invention are furnace carbon black, acetylene black, and channel black. These carbon blacks can be used either

alone or as an admixture of two or more. In order to obtain a moulded thermoplastic resin article having superior electrical properties, the use of a high structure-type furnace carbon black or acetylene black is preferred. A suitable average particle size for the carbon black is from 10 mμ to 100 mμ.

A moulded plastics article prepared from a thermoplastic resin composition containing less than 5% by weight of carbon black does not possess superior electrical properties since the carbon black cannot be dispersed in a state which promotes a sufficient improvement in its electrical properties. On the other hand, the mouldability of a thermoplastic resin composition containing carbon black in an amount greater than 70% by weight is reduced, and the mechanical and other properties of moulded articles obtained from it tend to be impaired.

Moulded articles can be prepared from the thermoplastic resin composition in accordance with the present invention by first admixing an olefin resin, another thermoplastic resin, and carbon black (the resins being in a powdery or pelletized form) in specific proportions, uniformly mixing them using a mixer such as a V-type blender to form a resin composition in accordance with this invention, if desired, premoulding the composition into pellets, for example, by means of extrusion moulding, and then moulding the composition into a plate, a sheet, a tubular, a tape or a film form by any desired methods such as an injection-moulding method, a compression-moulding method, a T-die-extrusion method, or an inflation-extrusion method. A suitable moulding temperature and pressure to employ is from 200 to 280° C and 50 to 150 kg/cm²G, respectively.

Figure 1 of the accompanying drawings is an electron photomicrograph (magnification 20,000 X) of a moulded plastics article prepared from a thermoplastic resin composition in accordance with this invention and consisting of polypropylene, polycapramide and furnace carbon black. In this photograph, the black portion shows the carbon black dispersed selectively in the polypropylene phase, and the white portion shows a polycapramide phase having poor affinity for the polypropylene and the carbon black. As can be seen from the photograph, the polypropylene phase and the polycapramide phase form a separated network structure, and the carbon black is selectively dispersed in the polypropylene phase which has good affinity for the carbon black. On the other hand, the carbon black is scarcely dispersed in the polycapramide phase. This white portion is confirmed to be a polycapramide phase from the fact that when the moulded article was dyed with an acid dye, only this white portion was coloured.

Characteristic features of the thermoplastic resin composition of this invention are as follows: firstly, carbon black is selectively dispersed only in the polyolefin resin phase which has good affinity for the carbon black; and secondly, the polyolefin resin phase forms a continuous phase in the resin matrix, whereby a conducting path based on carbon black is formed very effectively, and the use of a small amount of carbon black can give rise to good electrical conductivity. Since the addition of only a small amount of carbon black affords a high filling efficiency, this contributes to the improved mouldability of the above thermoplastic resin composition and also to a marked improvement in the mechanical and electrical properties of articles moulded from the composition. If either one of the above two factors is lacking, the beneficial effects of the thermoplastic resin composition of this invention cannot be obtained.

Since articles moulded from the thermoplastic resin composition of this invention have the unique structure described above, they have excellent electrical properties as demonstrated by the fact that their volume inherent resistivity is 1/10 to 1/30 of that of any electrically-conductive moulded plastics articles previously developed. In other words the moulded plastics articles of this invention have a volume intrinsic resistivity of from 5 to 100, preferably from 10 to 50, Ω-cm. Furthermore, these moulded plastics articles have superior fatigue-resistance even when used at high temperatures, and their volume inherent resistivity does not change greatly when there is a slight change in temperature during use. Even when the thermoplastic resin composition of this invention contains a relatively large amount of carbon black within the above-specified range, the mouldability of the composition is very good as compared with conventional thermoplastic resin compositions for preparing electrically-conductive moulded plastics articles, since the unique structure as described above arises during its moulded process.

The excellent electrical properties of moulded plastics from the thermoplastic resin composition of this invention make them especially useful as materials for an apparatus for preventing or removing static build-up in objects susceptible thereto. For example, by wrapping such a moulded article in the form of sheet, tape or film directly around the object or bonding it thereto, various difficulties ascribable to the generation of static electricity can be eliminated.

The following Examples are given to further illustrate the present invention in greater detail; unless otherwise indicated, all parts, percentages and ratios are given by weight.

### EXAMPLE 1.

Isotactic polypropylene powder having an intrinsic viscosity [η], as measured in tetralin at 135° C, of 1.37, nylon-6 powder having

an intrinsic viscosity [$\eta$], as measured in metacresol at 25° C, of 1.58, and furnace carbon black were uniformly mixed in the amounts specified in Table 1 using a V-type blender. The mixture was kneaded and extruded using a monoaxial screw extruder with a screw diameter of 30 mm and an L/D ratio of 25 while maintaining the temperature of the resin at 230° C to form pellets. The pellets were molded using a screw-type injection molding machine with a screw diameter of 45 mm while maintaining the temperature of the resin at 250° C, and that of the mold at 100° C to form specimens for measurement of the properties shown in Table 1. The volume inherent resistivity, the Izod impact strength, the tensile strength, the flexural strength, and the moldability were measured, and the results obtained are shown in Table 1.

For comparison, a resin composition containing polypropylene and furnace carbon black in a mixing ratio of 7/3 and 6/4, respectively, was prepared, and specimens were prepared under the same conditions as described above except that the temperature of the resin at the time of injection molding was maintained at 230° C. The above properties were measured, and the results obtained are also shown in Table 1.

Table 1.

| Run No. | Composition (wt.%) Polypro-pylene | Nylon-6 | Carbon Black | Volume Inherent Resistivity (Ω-cm) | Izod Impact Strength (kg-cm/cm²) | Tensile Strength (kg/mm²) | Flexural Strength (kg/mm²) | Mold-ability |
|---|---|---|---|---|---|---|---|---|
| 1 (invention) | 42.8 | 28.6 | 28.6 | 19.3 | 1.2 | 2.5 | 5.8 | O |
| 2 (comparison) | 70 | — | 30 | 406 | 0.8 | 1.9 | 5.1 | O |
| 3 (comparison) | 60 | — | 40 | 18.7 | 0.5 | 1.6 | 3.7 | X |

Note: O means good moldability.

The volume inherent resistivity was measured on a flat specimen of a size of 110×110×3.2 mm. The volume inherent resistivity was calculated from the resistivity value measured at 20° C under a pressure of 50 kg/cm² using a Wheatstone bridge where the flat specimen of the size of 110×110×3.2 mm was put between two cylindrical brass electrodes of a diameter of 8 cm. The Izod impact strength was measured using the method of ASTM D—256 on a notched rectangular specimen having a size of 12.5×63.7×6.4 mm. The tensile strength was measured using the method of ASTM D—638 on a No. 1 dumbbell specimen with a size of 19.3×216.6×3.2 mm. The flexural strength was measured using the method of ASTM D—790 on a rectangular specimen with a size of 12.5×127.4×3.2 mm.

It can be seen from the results shown in Table 1 that the thermoplastic resin composition obtained by this invention had good mouldability, and moulded articles obtained from this composition have excellent electrical conductivity and mechanical properties.

### EXAMPLE 2.

The same polypropylene powder and nylon-6 powder as used in Example 1 were mixed in the ratios shown in Table 2. The mixture was further mixed with furnace carbon black in an amount of 30% by weight. Specimens were prepared in the same way as in Example 1, and their volume inherent resistivity was measured in the same way as in Example 1. The results obtained are shown in Table 2.

Table 2.

| | Run Number | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition (wt.%) | 1* | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12* | 13* |
| Polypropylene | 100 | 95 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 4 | — |
| Nylon-6 | — | 5 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 96 | 100 |
| Volume Inherent Resistivity (Ω-cm) | 406 | 47.3 | 17.9 | 17.4 | 16.5 | 15.8 | 10.9 | 17.7 | 24.4 | 26.8 | 36.4 | 150 | 550 |

Note: Run Nos. 1, 12 and 13 marked by the asterisks are comparison runs, while the other runs are within the scope of this invention.

It is clear from the results shown in Table 2 that moulded articles prepared from the thermoplastic resin composition in accordance with this invention had superior electrical conductivity.

### EXAMPLE 3.

70 parts by weight of the same polypropylene as described in Example 1 were mixed with 30 parts by weight of each of the thermoplastic resins shown in Table 3, and the mixture was further mixed with 30% by weight of furnace carbon black to form a thermoplastic resin composition. The resulting composition was injection moulded under the conditions shown in Table 3 using a screw-type injection moulding machine with a screw diameter of 45 mm to form specimens. The volume inherent resistivity of each of the specimens was measured in the same way as in Example 1. The results obtained are shown in Table 3.

The polyethylene used had an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C, of 0.68. The polystyrene used had an intrinsic viscosity $[\eta]$, as measured in methyl ethyl ketone at 25° C, of 0.9. The poly(methyl methacrylate) used had an intrinsic viscosity $[\eta]$, as measured in chloroform at 25° C, of 0.6.

Table 3.

| Run No. | Resin Composition: Polypropylene | Resin Composition: Thermoplastic Resin | Extrusion Temperature (°C) | Injection Molding Temperature (°C) | Volume Inherent Resistivity (Ω-cm) |
|---|---|---|---|---|---|
| 1* | Yes | — | 230 | 230 | 406 |
| 2* | — | Nylon-6 | 230 | 250 | 550 |
| 3 | Yes | Nylon-6 | 230 | 250 | 16.5 |
| 4* | — | Polyethylene terephthalate | 270 | 270 | 72.6 |
| 5 | Yes | Ditto | 270 | 270 | 18.0 |
| 6* | — | Polystyrene | 230 | 230 | 620 |
| 7 | Yes | Ditto | 230 | 230 | 18:7 |
| 8* | — | Poly(methyl methacrylate) | 230 | 230 | 1200 |
| 9 | Yes | Ditto | 230 | 230 | 23.8 |

Note: Run Nos. 1, 2, 4, 6 and 8 marked by the asterisks are comparison runs, and the other runs are within the scope of this invention.

### EXAMPLE 4.

Example 3 was repeated except that high density polyethylene having an intrinsic viscosity [$\eta$], as measured in tetralin at 135° C, of 1.4 was used instead of the polypropylene.

The resulting specimens were examined for volume inherent resistivity in the same way as in Example 1. The results obtained are shown in Table 4.

Table 4.

| Run No. | Resin Composition: Polyethylene | Resin Composition: Thermoplastic Resin | Volume Inherent Resistivity (Ω-cm) |
|---|---|---|---|
| 1* | Yes | — | 138 |
| 2* | — | Nylon-6 | 550 |
| 3 | Yes | Ditto | 18.2 |
| 4* | — | Polyethylene terephthalate | 72.6 |
| 5 | Yes | Ditto | 19.5 |
| 6* | — | Polystyrene | 620 |
| 7 | Yes | Ditto | 20.5 |
| 8* | — | Poly(methyl methacrylate) | 1200 |
| 9 | Yes | Ditto | 25.1 |

Note: Run Nos. 1, 2, 4, 6 and 8 marked by the asterisks are comparison runs, and the other runs are within the scope of this invention.

### EXAMPLE 5.

Example 1 was repeated except that high structure-type acetylene black was used instead of the furnace carbon black. The resulting specimen was examined for volume inherent resistivity in exactly the same way as in Example 1, and was found to have a volume inherent resistivity of 13.4 Ω-cm. This demonstrated its superior electrical conductivity.

### EXAMPLE 6.

A resin composition (A) of 42% by weight of polypropylene, 28% by weight of nylon-6 and 30% by weight of furnace carbon black as in Run No. 6 of Example 2 was molded in the same way as in Example 1 to form Specimen (A). Furthermore, a resin composition (B) of 42% by weight of chloroprene rubber, 28% by weight of butyl rubber and 30% by weight of furnace carbon black, and a resin composition (C) of 42% by weight of polypropylene, 28% by weight of butyl rubber and 30% by weight of furnace carbon black were each kneaded using rolls, and press-formed to prepare Specimens (B) and (C), respectively.

The volume inherent resistivity, the tensile strength and the flexural strength of each of these Specimens (A), (B) and (C) were measured in the same way as in Example 1. The results obtained are shown in Table 5.

Table 5.

| Run No. | Specimen | Resin Composition | Volume Inherent Resistivity | Tensile Strength | Flexural Strength |
|---|---|---|---|---|---|
| | | | (Ω-cm) | ($kg/mm^2$) | ($kg/mm^2$) |
| 1 | (A) | Polypropylene + nylon-6 | 15.8 | 2.5 | 5.7 |
| 2* | (B) | Chloroprene rubber + butyl rubber | 98 | 0.5 | 0.8 |
| 3* | (C) | Polypropylene + butyl rubber | 402 | 1.1 | 1.5 |

Note: Run Nos. 2 and 3 are comparison runs.

The temperature dependence of the volume inherent resistivity of each of the Specimens (A), (B) and (C) was measured, and the results obtained are shown in Figure 2 of the accompanying drawings, which is a graph of volume inherent resistivity (Ω-cm) vs. temperature (° C).

As can be seen from the results shown in Figure 2 and Table 5, Specimen (A) prepared from the thermoplastic resin composition of this invention had superior mechanical properties and electrical conductivity, and in particular, exhibited stable electrical characteristics with a reduced extent of changes in volume inherent resistivity according to changes in temperature. This is due to the fact that polypropylene has good affinity for carbon black and the carbon black is selectively dispersed in the polypropylene resin phase. On the other hand, Specimens (B) and (C), no network structure was formed in which the carbon black was dispersed selectively in a specific resin phase, and therefore, the electrical conductivity of each of these specimens was lower.

WHAT WE CLAIM IS:—

1. A mouldable, electrically conductive thermoplastic resin composition comprising (A) 95 to 30% by weight of a resin composition consisting of (i) 100 parts by weight of a polyolefin resin having good affinity for carbon black and (ii) 5 to 900 parts by weight of a thermoplastic resin having poor affinity (as herein defined) for the polyolefin resin and for carbon black, said thermoplastic resin being at least one of a polyamide, a polyester, polystyrene, and poly(methyl methacrylate); and (B) 5 to 70% by weight of carbon black.

2. A composition as claimed in Claim 1, wherein said polyolefin resin comprises at least one homopolymer and/or co-polymer of an olefin monomer having 2 to 5 carbon atoms in the main chain.

3. A composition as claimed in Claim 2, wherein the olefin monomer is ethylene and/or propylene.

4. A composition as claimed in any preceding Claim, wherein said carbon black comprises at least one of furnace carbon black, acetylene black and channel black.

5. A composition as claimed in Claim 4, wherein said carbon black is furnace carbon black and/or acetylene black.

6. A composition as claimed in Claim 4 or 5, wherein said carbon black has an average particle size of from 10 mμ to 100 mμ.

7. A composition as claimed in Claim 1 and substantially as herein described.

8. A thermoplastic resin composition substantially as hereinbefore described with reference to any one of Run 1 of Example 1, Runs 2 to 11 of Example 2, Runs 3, 5, 7 and 9 of Example 3 and of Example 4, Example 5 and Run 1 of Example 6.

9. An article moulded from a thermoplastic resin composition as claimed in any preceding Claim.

10. An article as claimed in Claim 9 and having a volume inherent resistivity of from 5 to 100Ω-cm.

11. An article as claimed in Claim 10 and having a volume inherent resistivity of from 10 to 50Ω-cm.

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1457157 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

*FIG. 1*

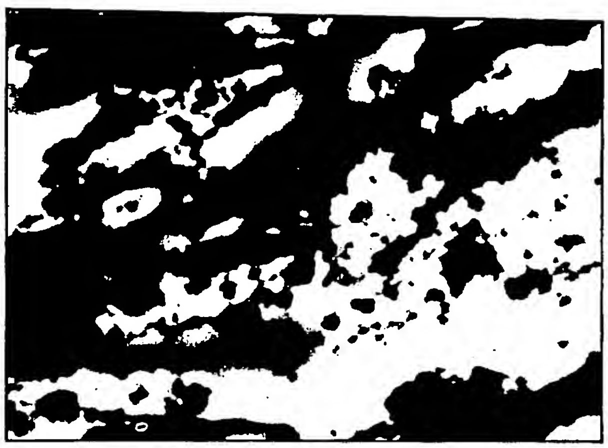
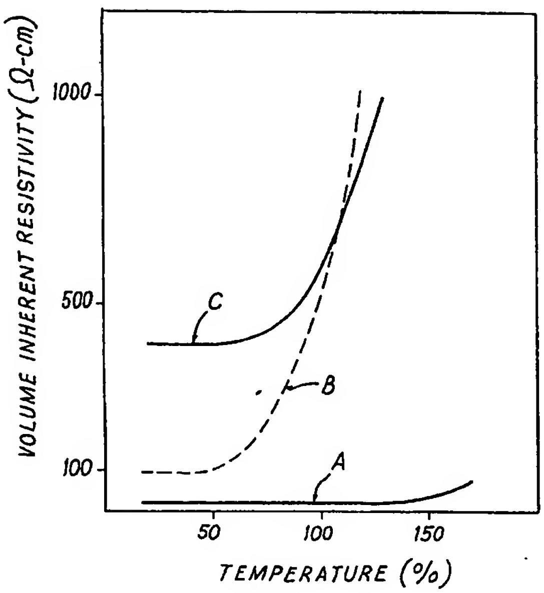


FIG. 2


VOLUME INHERENT RESISTIVITY (Ω-cm)
1000
500
100
C
B
A
50
100
150
TEMPERATURE (%)